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## SOME OBSERVATIONS OF THE EFFECT OF OZONE ON ALGAE GROWTHS

By S. T. POWELL

For the past five years the Baltimore County Water and Electric Company, under the supervision of Mr. A. E. Walden, has been using ozone as a sterilizing agent to purify their Herring Run water supply. The system as it was originally installed did not accomplish the results that were expected in many ways, so that it became necessary to entirely redesign the plant several times and this has necessitated much research, as little information could be obtained from any of the European plants in operation. It is not, however, the object of this paper to recite the details of the work that has been done, but merely to relate the effect of ozonization upon certain types of micro-organisms.

Herring Run is a small surface water stream that flows for the most of its course through a thickly populated territory and receives more or less surface drainage, so that there is always an appreciable amount of matter carried in suspension by the supply. Before reaching the ozone plant the water is stored for about twenty-one days in two earthen reservoirs from which a portion, but not all, of the top soil was removed before they were placed in use. Algae and other vegetable growths have always been more or less prolific in the supply and it has been necessary to treat the water many times each year with copper sulphate to keep down these objectionable growths. Up to the present time the water flowed to the ozone plant direct from the reservoirs without prefiltration and for this reason we have been afforded an opportunity to note the effect of ozone as an algacide.

The method of mixing the ozone and water is by means of aspiration, the falling water sucking the ozone directly from the generators, and is carried through a mixing chamber and from there delivered to the suction well of the pump. This well is open to the atmosphere so that the ozone not used up during passage through the mixing chamber is allowed to escape at this point.



It was noticed that very soon after putting the plant in operation a foamy greenish scum collected on the surface of the water, which increased in thickness the longer the plant operated and had to be removed by overflowing the well. Microscopic examination showed that the accumulation was due to algae growths to which had adhered small bubbles of ozonized air and had carried the organisms to the surface of the water. It was evident also that the ozone had a disintegrating effect on many of the organisms, especially the chlorophyceae and cyanophyceae. The analyses of samples of water before and after ozonization showed that the treatment had materially reduced the total number of organisms, as well as the amorphous matter. The percentage removal varied from day to day but not uniformly with the changes in the ozone concentration. It was evident that although the reduction showed the extent to which the organisms were eliminated from the water, this was by no means due entirely to oxidation by the ozone, but partly on account of breaking up of the more delicate organisms by the violent agitation of the water in passing through the mixing chamber, and to the formation of scum on the surface of the water in the suction well.

For this reason laboratory tests were made to determine to what extent the algae were killed by direct contact with the gas, and the general effect on the water resulting from ozonization of samples impregnated with such vegetable growths, especially with reference to color and odor.

#### LABORATORY TESTS AND APPARATUS

For this work an air ozone generator was used, the top of which was removed and replaced with a tightly fitting hood from which the ozone could be drawn without dilution from the air of the room. The general arrangement of the apparatus used is shown in chart I. One-half a liter of water to be tested was placed in the absorption bottle *B* and the ozone generated in *A* was aspirated through the bottle by means of the nozzle *C*. Only low concentrations (0.20 to 0.30 gram per cubic centimeter) could be obtained from the generator used, but in our experiments we have noted that low concentration and long contact will usually ensure as thorough oxidation of organic matter as higher concentration and short periods of contact. The ozone was drawn through the water at the rate of one liter per minute so as to prevent violent agitation, which would break up the algae.



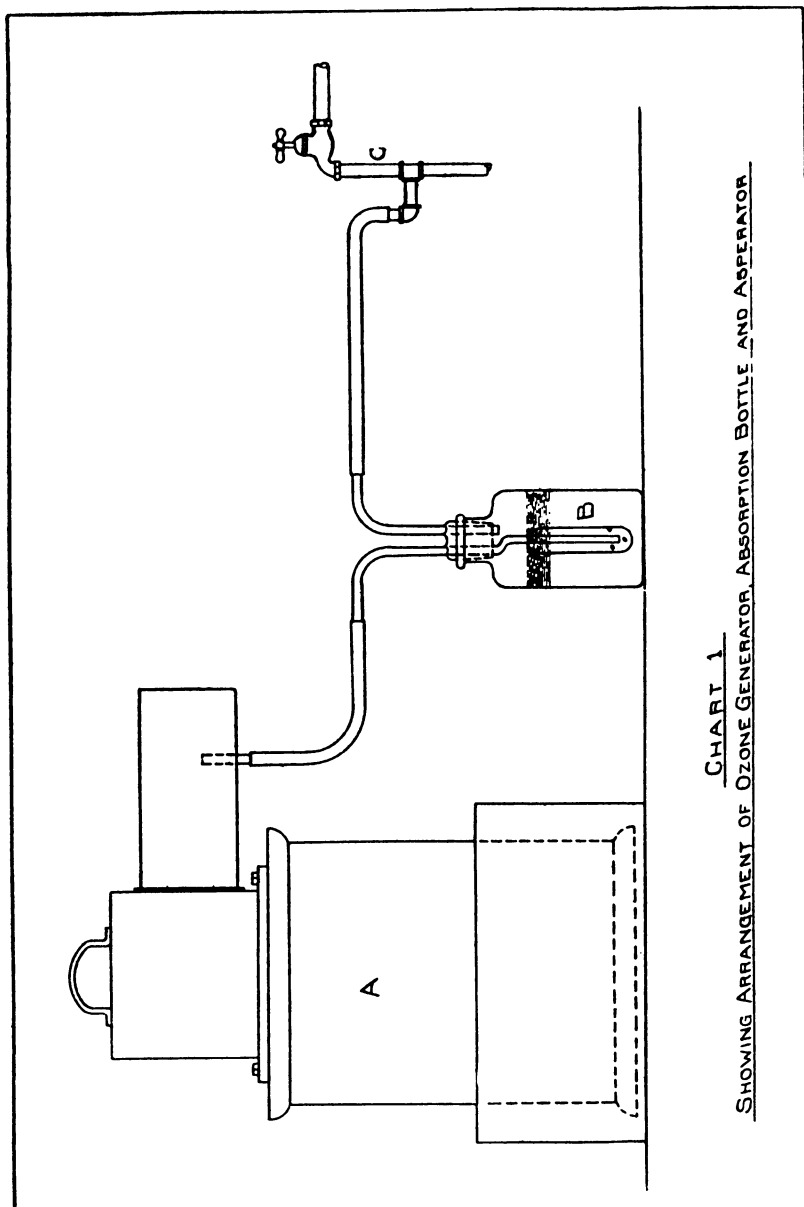




TABLE I

*Average percentage removal of micro-organisms effected by the ozonization plant of the Baltimore County Water and Electric Company*

|                       | <i>per cent</i> |
|-----------------------|-----------------|
| Diatomaceae.....      | 48.0            |
| Cyanophyceae.....     | 55.0            |
| Chlorophyceae.....    | 64.0            |
| Fungi.....            | 46.2            |
| Protozoa.....         | 41.5            |
| Rotifera.....         | 32.8            |
| Crustacea.....        | 30.0            |
| Amorphous matter..... | 41.0            |

Samples of swamp water were ozonized for one-half hour and then examined microscopically. There appeared to be a general disintegration of all the organisms containing chlorophyll and excepting where these growths were massed in bunches they were killed. The chlorophyll was scattered through the water but apparently the ozone had but a slight, if any, bleaching effect upon it. The diatoma, crustacea and protozoa were unaffected. After ozonization the samples were set aside for twenty-four hours and again examined. By this time the crustacea and protozoa were all dead but not removed; the color of the water had increased and there was a decided increase in the odor. The killing of the crustacea was probably due not to the oxidizing effect of the ozone but on account of the removal of the food supply by sterilization of the water. The color and odor increase was caused by the scattering of the chlorophyll and oil globules through the water when the organisms were broken up.

In support of this theory of the color increase a weak gasoline solution of pure chlorophyll was made up and through this ozone was passed for five hours. Even after this long period of contact there was not the slightest reduction in the color of the solution. The same concentration of ozone in twenty minutes removed 75 per cent of the color in a sample of water which had been stained by boiling a quantity of dead leaves in distilled water and then filtering.

#### ODORS

There has been much discussion recently in reference to the removal of odors by ozonization, but practically all of the investigations have been directed to the elimination of malodorous compounds that exist in the atmosphere so that the removal of odors in solution



touches a somewhat different phase of the subject. An attempt was made in this investigation to determine the general effect of ozonization in reference to odor removal from water, particularly those odors arising from algae growths. It was demonstrated from the tests that where the ozone acted upon the water containing living micro-organisms the characteristic odors were intensified. This condition was due to oxidation and disintegration of the plant and scattering the oil globules through the solution. These oily substances were only acted upon after complete oxidation of the organic matter present. In view of this fact waters containing micro-organisms were first filtered before attempting to deodorize them with ozone. At the time of conducting these tests it was not possible to obtain samples of water giving all the characteristic odors of the various forms of algae growths, but a number of substances that impart a distinctive odor were mixed with samples of tap water and the deodorizing effect of the ozone was noted. The data obtained from the tests, although they do not give any positive evidence of the ability of ozone to remove all odors arising from micro-organisms, gives some idea of the value of the gas as a deodorizer for water impregnated with such objectionable substances.

1. A distinctive algae odor arising from a sample of stagnant swamp water was greatly reduced in ten minutes with an ozone concentration of 0.20 gram per cubic meter and completely removed in thirty minutes. The same odor was entirely eliminated by a concentration of 1.69<sup>1</sup> grams in one minute.

2. A faint fishy odor caused by algae growths was removed in ten minutes with a concentration of 0.18 gram of the ozone gas.

3. Oil of rose dissolved in water imparting a distinct odor to the samples was but little affected after ten minutes of ozonization with a concentration of 0.20 gram, but almost entirely removed in thirty minutes of continuous ozonization at this same concentration. A concentration of 1.69 grams removed the odor in ten minutes.

4. Essence of heliotrope was acted upon in about the same manner as oil of rose, excepting that it was somewhat more easily removed by the high concentration.

<sup>1</sup>Where concentrations greater than 0.20 gram are reported they were obtained from the Herring Run ozonizers. It is possible with the generators at Herring Run to obtain concentrations as high as 5 grams per cubic meter. Concentrations higher than this are not economical as the ozone is not all used in passing through the sterilizers.



5. A few drops of oil of cloves in a half liter bottle was apparently unaffected by ozone at 0.20 concentration after one-half hour continuous contact. A concentration of 1.69 turned the samples a deep yellow and then red. The odor was greatly intensified during the first few minutes but lost its characteristic odor and imparted a very disagreeable woody odor to the solution.

6. Oil of wintergreen acted similarly to oil of cloves but did not lose its characteristic odor even in one-half hour using a concentration of 1.69 grams of ozone.

7. Oil of peppermint acted as did wintergreen, not being reduced in one-half hour of continuous ozonization. It was noted also that the ozone caused a bluish smoke to be generated when acting upon the peppermint, similar to the effect of this gas upon turpentine.

8. Mercaptan in dilutions of approximately one to one million was unaffected, showing no material reduction in the intensity of the odor arising from it.

9. Skatol in dilutions of 1 to 500,000 was not reduced with one concentration of 0.20 gram in thirty minutes. Higher concentrations were not employed.

10. Fecal odors from greatly diluted bacterial cultures were not reduced with concentrations of 0.20 gram. Higher concentrations were not tried.

11. The odor from oil of violets dissolved in water was slightly reduced in ten minutes with a concentration of 0.20 and entirely removed in thirty minutes. Ozone concentrations of 1.69 removed it in ten minutes.

12. A solution of tannic acid was greatly increased in color and odor by two minutes' ozonization and a concentration of 0.20 gram of the gas. This condition is one of considerable importance as it demonstrates one of the serious difficulties of color removal encountered in the operation of ozone sterilization.

#### CONCLUSION

The observations that have been made demonstrate clearly that certain forms of algae are very readily removed from water by direct oxidation while certain other forms are entirely unaffected even with protracted periods of contact with the ozone. In addition to this it has been noted that there is an increase in the odor arising from direct ozonization of algae that can only be removed after complete oxidation of the organic content of the water.



As has previously been stated, these studies were undertaken not with the idea of making use of ozone as an algacide but to determine what influence such growths would have in maintaining the efficiency of the sterilization plant, and to this extent the experiments have been of considerable value.

At practically all ozone water sterilization plants abroad the raw water supplies are filtered previous to treatment so that the influence of algae upon the efficiencies of the systems has not been studied. As the rate of filtration used at all these places is about the same as employed by mechanical filters in this country it is reasonable to suppose that practically all of the organisms are removed by the filter beds, but there is a possibility of the growth of organisms in the underdrains and conduits of the system, the presence of which will reduce the efficiency of sterilization in proportion to their abundance.

The ability of ozone to remove or reduce certain odors arising from substances dissolved in water is to the mind of the writer one of great importance. There is no doubt that ozone is a powerful deodorizing gas under certain conditions and when brought into direct contact with the substance for a sufficient period. Its deodorizing value depends on the oxidizability of the substance treated, and concentration of the gas as well as the thoroughness of the mix.